

AD-A011 398

CORROSION FATIGUE OF CU AND CU 7.8% Al

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Prepared for:

Army Research Office

December 1974

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ANC-10091.1-MS	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) CORROSION FATIGUE OF Cu AND Cu 7.8% Al		5. TYPE OF REPORT & PERIOD COVERED Final Report 1 Mar 74 - 31 Aug 74
7. AUTHOR D. J. Duquette		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Rensselaer Polytechnic Institute Materials Engineering Department Troy, New York 12181		8. CONTRACT OR GRANT NUMBER(s) DAHCO4 74 C 0015
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Box W, Duke Station Durham, North Carolina 27706		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE December, 1974
		13. NUMBER OF PAGES 8
		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) UNCLASSIFIED		
18. SUPPLEMENTARY NOTES The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents.		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Corrosion Fatigue Cyclic Deformation		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Transmission electron microscopy of pure copper exposed to air and to corrosive solutions under cyclic stresses shows that corrosion effectively "softens" metal surfaces by destroying the dislocation cell structure and preventing its reformation, thus resulting in accelerated slip. Additionally the preferential corrosion of surface slip offsets and grain boundaries results in grooving of these areas and rapid intergranular crack initiation and similarly studies of Cu 7.8% Al alloy single crystals shows corrosion to be specifically associated with surface slip offsets.		

AD A011398

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Final Report for the period 3/1/74-8/31/74

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30 December 1974

U. S. Army Research Office
Contract DAHCO4 74 C 0015

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CORROSION FATIGUE OF Cu AND Cu 7.8% Al

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Abstract

Transmission electron microscopy of pure copper exposed to air and to corrosive solutions under cyclic stresses shows that corrosion effectively "softens" metal surfaces by destroying the dislocation cell structure and preventing its reformation, thus resulting in accelerated slip. Additionally the preferential corrosion of surface slip offsets and grain boundaries results in grooving of these areas and rapid intergranular crack initiation and propagation.

Similarly, studies of Cu 7.8% Al alloy single crystals shows corrosion to be specifically associated with surface slip offsets, resulting in an accentuated notch-peak topography, consequent stress concentration, and early crack initiation. The role of cyclic stress appears to be to provide fresh mobile dislocations to the free surface for preferential corrosion of these regions.

Copper

During the period 3/1/74 to 8/31/74 emphasis has been placed on transmission electron microscopy (TEM) of thin foils of surfaces of copper specimens which had been cycled in air, in 0.5N NaCl and in 0.5N NaCl with applied anodic currents. The object of this investigation has been to better understand the enhanced slip which was observed from previously replicated specimens. In order to prepare thin foils suitable for TEM, copper specimens were fatigued under the appropriate environmental conditions, plated with a thick copper plate (\approx 0.5cm), and transversely sectioned into disks. The disks were subsequently mechanically polished and finally electropolished with the edges covered with lacquer (window technique), until perforation occurred and progressed to the plate/specimen interface. While this method had a low success rate (approximately 1:10 foils with transparent areas in the proper locations) sufficient information was obtained to justify the time and effort involved.

As has been reported by other investigators, specimens fatigued in air show a well developed dislocation cell structure within 1% of total specimen life. This cell structure extends both to the specimen surface and to grain and twin boundaries with no appreciable difference in cell size or dislocation density in the cell walls. As cycling continues the cell walls become more defined ("tighter") and, dependent on grain orientation, appear to stabilize at a given diameter. It is interesting to note that, although most of the tests conducted were in

the high cycle to failure mode ($> 10^5$ cycles in tension-tension) the dislocation structure was shown to be cellular rather than the "raft and ladder" structure reported by Lukas and co-workers¹ (in tension-compression), indicating that the dislocation structure is stress (or strain) dependent rather than life dependent.

When cyclic stresses are applied in 3% NaCl, particularly with applied currents, significant changes are observed in the surface connected dislocation structure. The action of the corrosive medium "unravels" the dislocation cell structure adjacent to the metal surface. Cell walls show considerably lower dislocation densities and are broadened where they intersect the free surface of the metal. This behavior is accentuated during the early portions of fatigue life but appears to reach a steady state condition by approximately 10% of fatigue life. The "unravelling" process is greater with applied anodic currents and is further accentuated in the vicinity of grain and twin boundary intersections with the free surface.

These observations indicate that corrosive media in effect continuously soften the metal surface with respect to the interior and prevent localized cyclic hardening which is generally associated with cyclic stresses. Thus the free surface is continually in the process of attempting to form a stable cell structure without success. These observations explain the increase in slip step height and decrease in slip step density previously reported for this material under corrosion² fatigue conditions. Additionally the data may be extrapolated to

other materials since an enhanced intrusion/extrusion phenomenon has been observed in low carbon steels cyclically stressed in aggressive chloride solutions ³. The large number of mobile dislocations associated with continuous cell formation are also thought to be preferred sites for accelerated corrosion since slip step grooving has been observed. Additionally, grain boundary grooving has been reported in copper under corrosive conditions. The enhanced softening associated with grain/twin boundary surface intersections would indicate that these are preferential sites for corrosive attack.

In summary then, corrosion fatigue appears to be caused by a complex mechanism involving at least two interrelated phenomena: (1) cyclic softening of the surface which results in accelerated surface deformation, and (2) corrosive attack of strained material surrounding mobile dislocations which are continually being provided to the metal surface by the softening process. In pure soft materials such as copper this action results in a blunting of transcrystalline crack nuclei but also results in preferential attack of grain boundaries and subsequent intergranular failure. It may be speculated that intercrystalline failure is not observed in steels because grain boundary regions are more deformation resistant than grain interiors because of the normally observed increase in carbon content associated with grain boundaries. Intergranular crack initiation has been observed in relatively pure iron exposed to corrosion fatigue conditions ⁴.

Cu-7.8% Al

During the period 3/1/74 to 8/31/74 emphasis on this alloy system has been placed on attempting to understand the large increase in surface slip offset height and the highly damaging influence of corrosive environments on the fatigue behavior of these materials. Single crystals of Cu-7.8% Al have been prepared and fatigue tested in tension-tension in laboratory air, 0.5N NaCl solution and 0.5N NaCl solution with an applied anodic current of $200\mu\text{A}/\text{cm}^2$. A marked decrease in fatigue life was observed under free corrosion conditions and a still larger decrease in fatigue life under conditions of applied anodic currents. These results are significant since there was some question as to the nature of reduced fatigue resistance of these materials under corrosive conditions; polycrystalline materials exhibited primarily intergranular failures in aggressive environments.

In air, slip offsets are fine and closely spaced. Under free corrosion conditions, however, slip offsets show large increases in height and a reduction in density. Deep grooves are associated with slip bands, the grooves being broader for more severe corrosion conditions. Fracture surfaces of all single crystals were similar in appearance when viewed under a scanning electron microscope.

In comparing the results of the single crystal Cu-Al data with the electron microscopic data of the copper (polycrystals); the differences in slip character should be considered. It has been extensively shown that fatigued copper exhibits a distinctive cell

structure while low stacking fault energy Cu-Al alloys show co-planar dislocation substructures. In the alloy, surface slip offsets are generally much longer, straighter and more widely spaced than in the pure metal. If the mechanism proposed for pure copper is valid, it is to be expected that corrosive environments will have a larger effect on planar slip materials. Accordingly, aggressive environments will "soften" specific slip bands and allow increased slip to occur. At the same time, since specific slip systems will be highly active, other systems, which might otherwise require higher resolved stresses need not operate and strain will be concentrated in those bands which are active. Thus slip will be more intense while the observed slip band density will be reduced. Preferential corrosion can be expected to occur at emerging slip steps creating the notch-peak topography which is observed. This notch-peak topography can be expected to act as stress raising singularities which will accelerate crack initiation and early crack growth.

In summary, the corrosion fatigue process in the binary alloy is similar to that observed for the pure metal but is accentuated by the planarity of slip and subsequent highly localized corrosion in the alloy.

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